Environmental stress cracking
of thin high density polyethylene samples

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Fracture behaviour of thin HDPE samples tested in air and in presence of two bleach solutions was evaluated adopting a *J*-integral approach; material resistance after continuous exposure for a sufficient interaction time was reduced. Separate elastic and plastic contributions were determined, with the bleach solution mainly acting on the latter.

Introduction

High-density polyethylene (HDPE) is a polymer used for the containers of several household liquid detergents; during their service life they can interact with the polymeric material and affect its mechanical behaviour. Among the various mechanisms which can be activated by these products, Environmental Stress Cracking (ESC) may occur through the combined action of mechanical stress and the chemical itself; this purely physical phenomenon is related to local plasticization, craze/crack initiation and propagation and it can lead to the premature failure of the component.

Fracture mechanics had been used to study the ESC resistance of several polymers; considering polyethylene, in particular, it has been demonstrated that various detergents can reduce its fracture resistance [1-5]. Moreover, the effect of household bleach on thick samples of the same HDPE considered in this work had already been assessed in previous studies by the authors [6,7]. In this work, the fracture behaviour of thin blow-moulded samples directly obtained from bottles was investigated in air and in the presence of two bleach solutions; due to the reduced thickness of the specimens, the material was loaded under plane stress conditions and exhibited extensive plastic deformation before and after fracture initiation. The accuracy of the Linear Elastic Fracture Mechanics approach previously adopted could hence be limited and results were analysed following an elasto-plastic, *J*-integral based approach.

Materials and methods

Cylindrical bottles made of HDPE, having a monomodal molecular weight distribution, were produced via extrusion blow moulding and supplied by Fater S.p.A.

Double edge notched specimens in tension (DENT), having 35 mm width and 85 mm length, were cut along the longitudinal direction of the bottle. Notches, with a length of 7 mm, were introduced by hand-sliding a razor blade having a tip radius lower than 5 μm. Specimens were gripped so that the effective testing size was 35 x 35 mm.

Fracture tests were performed at 60°C on an Instron 1185R5800 electro-mechanical dynamometer equipped with a 10 kN load cell. Constant displacement rates ranging from 10 to 0.0007 mm/min were applied; tests were first conducted in air and subsequently, thanks to the use of a custom-designed chamber (see [8] for further details), in two different solutions:

• Sol. A was an aqueous solution of sodium hypochlorite, sodium hydroxide, sodium carbonate, surfactants and perfume (similar to commercial bleach products);

• Sol. B had the same composition, except for sodium hypochlorite which was replaced by water.

Visual detection of fracture initiation wasn't possible in the considered environments because they were opaque. The indirect determination of crack initiation via the load separation method, initially developed for metals in [9] and subsequently extended to polymers

[10, 11], was attempted; however applying load-separation to HDPE data gave unreliable results. Therefore, the maximum of the load-displacement curve was considered as a fracture initiation criterion. This allowed for an objective determination of initiation with a reasonable amount of data scatter.

The corresponding value of J-integral was calculated according to [12]:

$$J = J_{el} + J_{pl} = \eta_{el} \frac{U_{el}}{B \cdot (W - a)} + \eta_{pl} \frac{U_{pl}}{B \cdot (W - a)} \tag{1}$$

in which J_{el} and J_{pl} are the elastic and plastic contribution to J; η_{el} and η_{pl} are the elastic and plastic shape factors (which for the considered geometry are equal to 0.661 and 0.683 respectively); B is specimen thickness; $W - a$ is the ligament; U_{el} and U_{pl} are the elastic and plastic components of the total energy absorbed by the specimen up to the maximum of the load-displacement curve. To compute these two quantities, the area under the load-elastic displacement and the load-plastic displacement curves, P-u_{el} and P-u_{pl} respectively, was evaluated. u_{el} was computed according to Equation (2):

$$u_{el} = P \cdot C_0 \tag{2}$$

in which C_0 is the initial sample compliance. Subtracting this elastic displacement from the global displacement u gave the plastic displacement, u_{pl}. The results of the fracture tests were reported in terms of J vs. initiation time curves.

After the tests, the ligament of selected specimens was observed using an Olympus SZ40 stereomicroscope.

Results and discussion

The results of the tests conducted in the three environments are reported in Figure 1 (a). The calculated J value at initiation in air does not seem to vary much within the explored range. For what concerns the tests conducted in presence of the two active environments, instead, a marked decrease of this fracture parameter can be noticed, implying a significantly shorter time required for crack initiation for a given load. There is no difference between the two solutions demonstrating that, as already reported in [6, 7], sodium hypochlorite, which is the active ingredient of household bleach, does not affect the ESC resistance of the investigated HDPE. Moreover, the intersection point between curves obtained in air and in the two active environments can be easily determined confirming that a minimum interaction time is required to observe a gradual decrease in the fracture resistance of the polymer. In the case of thick samples of the same material, produced via compression moulding, this critical interaction time was approximately equal to 2600 s [7], which is one order of magnitude lower with respect to the present one. This discrepancy could be related to the different stress state and constraint level to which the material is subjected or to the different material structure generated by the two production processes. In particular, as revealed by DSC analysis, the crystallinity of the blow-moulded material (60%) is about 10% lower than that of the compression moulded one. Further, it must be noticed that the choice of the maximum of the load-displacement curve as the value of crack initiation could affect this result and, as a consequence, further analyses are required to clarify this point.

Looking at the elastic and plastic contributions to J during the tests in air, a difference of about one order of magnitude can be measured between J_{el} and J_{pl}. This indicates that the greatest part of the energy absorbed by the specimen is spent for plastic deformation; due to the presence of the two notches in the DENT sample, this is mainly localized in the region immediately surrounding the fracture process zone and not in the specimen bulk. In presence of the two active environments a decrease of both contributions was observed, significantly more pronounced for the plastic one; the difference with in-air values, as expected, increases for lower loads, meaning that the phenomenon is more severe when the solution has more time to interact with the polymer. The plastic strains in the ligament region are hence reduced and a more brittle failure mode is observed.
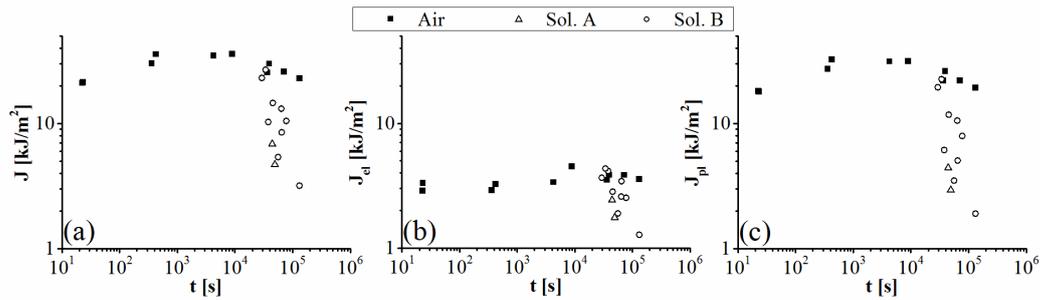
Figure 1: results of the fracture tests.
(a) global value of J; (b) elastic contribution; (c) plastic contribution.

These results are in agreement with post-mortem observations of the fracture specimens. The failure mode is significantly different in the two cases: specimens tested in air (Figure 2 (a)), display a greater extent of plastic deformation with respect to those tested in the active environments (Figure 2 (b)). In the latter case, the plastic deformation of the ligament was largely suppressed leading to a more brittle material failure. This fact is in accordance with the mechanism commonly proposed to explain the ESC phenomenon: in proximity of a craze ahead the crack tip, the active environment acts by locally plasticizing the polymer. This favours the disentanglement of macromolecules, thus promoting a more brittle failure, which in turn implies a lower amount of dissipated energy with respect to what was observed in air.
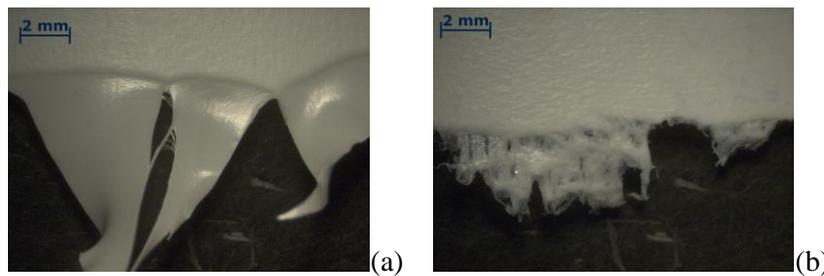

Figure 2: ligament of two samples after a fracture test at 0.005 mm/min.
(a) specimen tested in air; (b) specimen tested in Sol.B.

Conclusions

The fracture behaviour of thin blow moulded samples of HDPE was assessed in air and in presence of two household bleach solutions using a J-integral based approach.
After a minimum interaction time, the fracture resistance of the polymer was decreased by the active environments while it seemed that, as observed for thick samples of the same material, the presence of sodium hypochlorite did not influence this property.
The decomposition of J in its elastic and plastic parts and the visual inspection of the specimens revealed that the two solutions acted by suppressing the plastic deformation in the sample ligament and, consequently, decreasing the amount of energy required by this process. This mechanism is in agreement with the commonly accepted idea that, in presence of a craze, the active environment acts as a local plasticizer favouring the disentanglement of the polymer macromolecules and promoting a more brittle failure.

Acknowledgments

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